



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/783,386  
Applicants : Larry F. Rhodes et al.  
Filed : February 20, 2004  
Title : Dissolution Rate Modifiers for Photoresist Compositions  
Group Art Unit : 1752  
Examiner : Amanda C. Walke  
Confirmation No. : 6408  
Customer No. : 28989

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**DECLARATION UNDER 37 C.F.R. § 1.132**

Sir

1. I, Larry F. Rhodes, am one of the named inventors of the invention described and claimed in the above-identified application for letters patent.

2. I am a citizen of the United States and reside at 3036 Vincent Road, Silver Lake, OH 44224. I graduated from the University of North Carolina in 1980 with a B.S in chemistry and from Indiana University in 1984 with a Ph.D. in chemistry. From 1984-1986, I was a post-doctoral student at the Laboratorium für Anorganische Chemie, Swiss Federal Institute of Technology (ETH-Zentrum) in Zurich, Switzerland. From 1986-1988, I was a post-doctoral student in the Chemistry Department at The Ohio State University in Columbus, OH. From 1988 to 2001, I was employed by BFGoodrich Company. In 2001, Sumitomo Bakelite purchased this portion of BFGoodrich (to become Promerus Electronic Materials). From 2001 to the present, I have been employed with Promerus Electronic Materials, Research and Development Center in Brecksville, OH and am currently a research fellow.

3. I am the author/co-author of over eighty (80) technical articles and the inventor/co-inventor of over forty (40) patents/patent applications, the large majority of which being directed to the polymerization of norbornene-type monomers and the use of such polymers (see, Exhibit A).

4. I have read and am thoroughly familiar with the contents of the above-identified patent application, as well as the prior art cited by the Examiner, namely, Willson et al. (hereinafter "Willson") (Polymeric materials journal article) and U.S. Patent Application No. 2004/0265738 to Feiring et al.

5. By way of background, and as shown in the attachment denoted as Exhibit B, I attest that the International Union of Pure and Applied Chemistry (IUPAC) provides definitions of the terms "polymer" and "oligomer" that are unambiguous and distinct from one another.

6. Further, as shown in the attachment denoted as Exhibit C, I attest that photolithography, as employed in the manufacture of Integrated Circuits, uses a photoresist layer disposed over a substrate to form a three-dimensional relief image that is a replica of the opaque and transparent areas present on a mask or reticle; such replica serving to protect certain regions of the underlying substrate from the effects of a subsequent process. (See, C-1)

7. I attest that it is well known, as shown in Exhibit C at C-2 and C-3, that the essential attributes of a photoresist include: (1) uniform, defect-free films on a substrate, i.e., no precipitation, which is especially challenging for ultra-thin films; (2) sufficient adhesion and cohesion, which is achieved through exposure, bake, develop and transfer steps; (3) high radiation sensitivity, i.e., throughput; (4) high fidelity reproduction of mask, i.e., high resolution and contrast; (5) good etch resistance, i.e., pattern transfer; and (6) readily removed, i.e., stripped; and to achieve these attributes a photoresist composition includes one or more additives (in addition to the polymeric binder resin), such as base quenchers, plasticizers, dissolution rate modifiers and crosslinkers (negative tone); a photoacid generator also referred to as a photoacid compound (PAG or PAC); and a solvent (vehicle for application).

8. Additionally, I attest that when a person of skill in the art contemplates preparing a chemically amplified positive-tone resist binder resin, the following design considerations (among others) will be used: (1) hydrophilicity- for good positive tone development characteristics; (2) a high glass transition temperature (Tg) (130-170oC)- for good thermal properties and high post-exposure bakes; and (3) easily protected hydroxyl group- for

incorporation of acid-cleavable functionality. With regard to a high Tg, such is needed since chemically amplified resists need a bake step after the image-wise exposure step to induce thermal deprotection of protected acid groups to render the exposed region of the resist soluble in aqueous base. (See, C-4 and C-5) I further attest that it is common knowledge in the art of polymer chemistry that the molecular weight of a polymer has a direct effect on the polymer's Tg. In particular, Tg decreases dramatically below the "entanglement" molecular weight and polymers lose properties such as mechanical strength. (See, C-6)

9. I attest that as shown in Exhibit C, at C-7 and C-8, typical molecular weights for 248 nm photoresist binder resins usually range from 11,000 to 20,000, and as shown at C-9, it is well known that for 193 nm poly(methacrylate)-based binder resins, photoresist polymers of "low" molecular weight do not allow good imaging performance and therefore are unsuitable as photoresist polymeric binder resins.

10. Still further I attest that the present invention, recited in Claim 1, is directed to a dissolution rate modifier (DRM) and NOT a photoresist binder resin or composition. Further that such DRM comprises, among other things, cyclic olefin-based oligomers derived from monomers in accordance with one or more of Formulae A, B or C (which are norbornene-type monomers) and Formulae D or E (which are allylic-type monomers); where such oligomers have a weight average molecular weight ( $M_w$ ) of less than about 3,000.

***Therefore, I declare that:***

A. Willson discloses polymers that are employed as photoresist binder resins within photoresist compositions, whereas the claimed invention is directed to oligomers that are useful as dissolution rate modifiers (DRM) that may be added to a photoresist composition. That the structures shown in Fig. 4 of Willson are imaging polymers and while monomer structures, such as those in accordance with Formula A recited in Claim 1, might be used to form the aforementioned Willson polymers, one of ordinary skill in the art would certainly distinguish the photoresist polymer resins of Willson from the oligomeric dissolution rate modifiers of the present invention.

B. The differences between a polymeric binder resin such as disclosed by Willson, and an oligomeric DRM in accordance with the present invention, is readily seen by even the

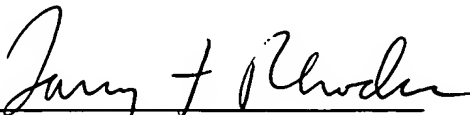
most casual observer ... yet alone a skilled artisan ... when both are cast onto a substrate, for example a silicon wafer (see, Exhibit C, C-11 and C-12). In particular, casting equal weight percent solutions of a polymer and an oligomer onto substrates to form films, results in films that have markedly different appearance and physical characteristics (see, the color fringing indicating poor uniformity for film formed from oligomer solution and the result after baking that the film thickness of the oligomer formed film decreases by greater than 75%, whereas the thickness of the polymer formed film decreases only by an average of 3%. Therefore, oligomeric DRMs cannot be used to form good quality films, and cannot be used as binder resins for photoresists, as disclosed in Willson. Indeed, the following citation of Hung et al. (citation # 4 in the cited Willson article) (Proceedings of SPIE, 2001, 4345, 385) indicates that Willson did not know, at the time the article was written and published, how to make oligomers, i.e., compounds having a molecular weight of less than 3,000:

“The use of typical chain transfer agents on the polymerization of monomer 9 was unsuccessful... Addition of 1-hexene did not reduce the molecular weight of the polymer to an acceptable degree...”

C. With regard to Feiring, such published application does not provide any disclosure regarding oligomers and never even mentions the term. Rather, like Willson, Feiring only speaks to polymers and methods for making.

Finally:

I declare further that all statements made herein of my own knowledge are true and that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application and any patent issuing thereon.

  
(Larry F. Rhodes)

Date 11/14/06

**Larry F. Rhodes****Publications**

1. "Optical Density at 193 nm of Vinyl Addition Poly(norbornene) Made Using Hydrogen as a Chain Transfer Agent", C. Chang, J. Lipian, C. Burns, L. F. Rhodes, R. Lattimer, manuscript in preparation
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Larry F. Rhodes

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Larry F. Rhodes

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## Exhibit 'A'

Larry F. Rhodes

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## Exhibit 'A'

Larry F. Rhodes

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## Exhibit 'A'

Larry F. Rhodes

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Larry F. Rhodes

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## MOLECULES AND MOLECULAR STRUCTURE

### 1.1 macromolecule

#### **polymer molecule**

A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

#### *Notes*

1. In many cases, especially for synthetic polymers, a molecule can be regarded as having a high relative molecular mass if the addition or removal of one or a few of the units has a negligible effect on the molecular properties. This statement fails in the case of certain macromolecules for which the properties may be critically dependent on fine details of the molecular structure.
2. If a part or the whole of the molecule has a high relative molecular mass and essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass, it may be described as either **macromolecular** or **polymeric**, or by **polymer** used adjectivally.

### 1.2 oligomer molecule

A molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass.

#### *Notes*

1. A molecule is regarded as having an intermediate relative molecular mass if it has properties which do vary significantly with the removal of one or a few of the units.
2. If a part or the whole of the molecule has an intermediate relative molecular mass and essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass, it may be described as **oligomeric**, or by **oligomer** used adjectivally.

### 1.3 monomer molecule

A molecule which can undergo polymerization thereby contributing constitutional units to the essential structure of a macromolecule.

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